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Molecular Rearrangements in the Camphor Series. Lauronolic Acid and Campholactone

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Molecular Rearrangements in the Camphor Series.

LAURONOLIC ACID

AND

CAMPHOLACTONE

BY

CHARLES ELDRID BURKE

A. B. McMaster University, 1907

A. M. McMaster University, 1909

THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

DOCTOR OF PHILOSOPHY

IN CHEMISTRY

IN

THE GRADUATE SCHOOL

OF THE

UNIVERSITY OF ILLINOIS

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THE GRADUATE SCHOOL

May 10th, 1911

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

CHARLES ELDRID BURKE

ENTITLED Molecular Rearrangements in the Camphor Series. Lauronolic Acid and Campholactone

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Doctor of Philosophy

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In Charge of Major Work

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197566

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Molecular Rearrangements in the Camphor Series

LAURONOLIC ACID

and

CAMPHOLACTONE

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The present work was undertaken in September 1909 at the suggestion of Professor W. A. Noyes, and has been carried on in the chemical laboratory of the University of Illinois under his supervision during the academic years 1909-10; 1910-11.

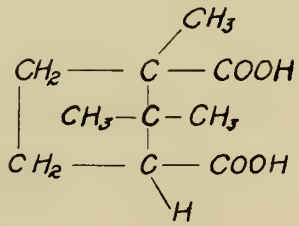
I wish to express my deep gratitude to Professor Noyes for his untiring patience and sympathetic assistance during the progress of this work.

I wish also to thank both Professor Noyes and Mr. R. S. Potter for access to the data of much unpublished work carried out in this laboratory.

MOLECULAR REARRANGEMENTS IN THE CAMPHOR SERIES.

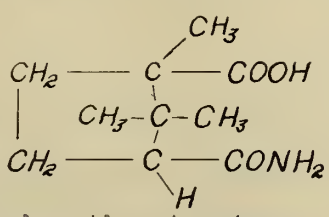
LAURONOLIC ACID AND CAMPHOLACTONE.

Komppa's synthesis has established the structure of camphoric acid as

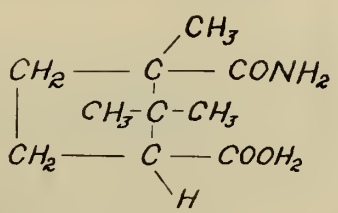


Since this structure contains an α or secondary and a β or tertiary carboxyl, it would lead us to expect two distinct series of compounds depending upon which carboxyl is substituted or eliminated.

Two such series have now been well established. Two camphoramidic acids are known, α camphoramidic, which has the structure



and β camphoramidic which has the structure



The first of these was obtained by Auwers and Schnell[1] on treating the anhydride of camphoric acid with strong ammonia: It has been obtained also by Claissen and Manasse[2] by heating isonitrosocamphor with fuming hydrochloric acid. The β camphoramidic has been prepared by Noyes[3] by the decomposition of camphoric imide with sodium hydroxide[#]. Both compounds are now well known and their structures have been fully established.

From these two acids Hoogewerf and VanDorp[5] obtained cyanlauronic acid an and dihydro-cyan-campholytic acid respectively. When α camphoramidic acid is treated with sodium hypobromite, it is converted into amino lauronic acid[6] the chloride of which can be isolated and crystallized; m. p. 303-305°. In an exactly analogous way, β camphoramidic is converted into dihydro-amino-campholytic, the chloride of which can also be isolated and purified. The chloride of this acid melts at 261-262° with decomposition, and differs markedly in crystalline structure from the chloride of amino-lauronic acid.

On treating the nitroso derivative of the anhydride of amino-lauronic acid with sodium hydroxide the following decomposition products have been obtained[7].

1. A liquid unsaturated acid, having the formula $C_8H_{13}COOH$, which resembled the acid of Fitting and Woringer, and was called γ lauronolic.

2. A crystalline unsaturated acid of the same empirical formula as the above; m. p. 152-154°.

3. A lactone, isomeric with the above acids, but melting at 32° and therefore not identical with the lactone of Fitting and Woringer.

- -

1. Ber., 26, 1522.
2. Ann., 274, 81.
3. Am. Chem. J., 16, 308.
This compound was prepared simultaneously and quite independently by Hoogewerf and VanDorp. Proc. Dutch acad. Jan. 27, 1894.
4. loc. cit.
5. Am. Chem. J., 16, 502.
6. Ibid, 16, 508; 32, 288; 35, 379.

4. Another isomeric lactone; m. p. 164-165° from which the corresponding hydroxy acid has been obtained.

5. Hydroxy lauronic acid.

6. A hydrocarbon laurolene, C_8H_{14}; b. p. 120-122°.

The decomposition of dihydro-amino-campholytic acid with sodium nitrite is seemingly not as complex as that of the amino-lauronic acid; a number of products are obtained here however which are quite analogous to those obtained in the lauronic series[7].

1. An unsaturated acid of the formula $C_8H_{13}COOH$;, α campholytic acid.

2. An isomeric lactone, campholyto lactone; m. p. 115-116° from which the corresponding hydroxy acid has been prepared.

3. An hydroxy acid, dihydro-hydroxy-campholytic acid.

4. A hydrocarbon isolaurolene, C_8H_{14}; b. p. 108-110°.

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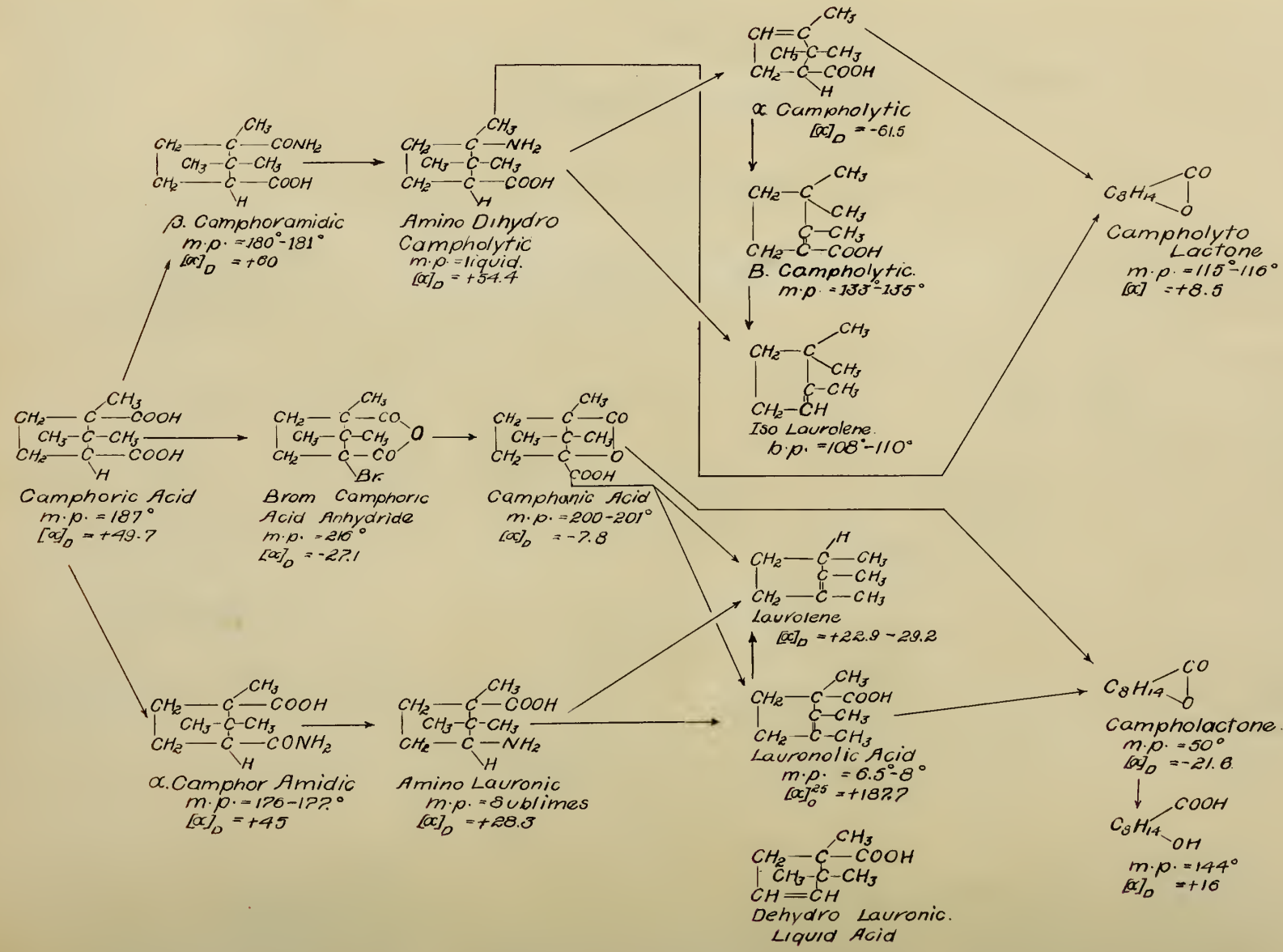
7. Ann. 314, 392; Am. Chem. J., 16, 307, 505; 17, 421; Ber. 33, 2935; Bull. Soc. Chim., 25, 81.

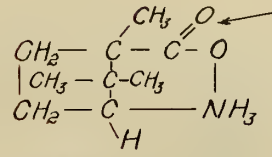

Camphoric Acid
m.p. = 187°
[α]D = +49.7
β. Camphoramidic
m.p. = 180°-181°
[α]D = +60
Amino Dihydro Campholytic
m.p. = liquid.
[α]D = +54.4
Brom Camphoric Acid Anhydride
m.p. = 216°
[α]D = -27.1
Camphanic Acid
m.p. = 200-201°
[α]D = -7.8
α. Campholytic
[α]D = -61.5
B. Campholytic.
m.p. = 133°-135°
Iso Laurolene.
b.p. = 108°-110°
Campholyto Lactone
m.p. = 115°-116°
[α] = +8.5
α. Camphor Amidic
m.p. = 176-177°
[α]D = +45
Amino Lauronic
m.p. = Sublimes
[α]D = +28.3
Laurolene
[α]D = +22.9 - 29.2
Lauronolic Acid
m.p. = 6.5°-8°
[α]25D = +18.7
Dehydro Lauronic. Liquid Acid
Campholactone.
m.p. = 50°
[α]D = -21.6
m.p. = 144°
[α]D = +16

α. OR LAURONIC SERIES.

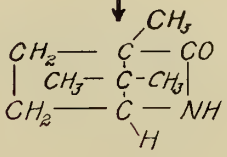
α Camphoramidic Acid.

↓

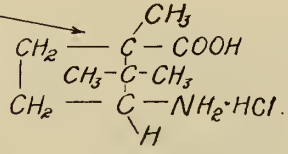
Amino Lauronic Acid.



Inner Anhydride.
m.p. = sublimes.
$[\alpha]_D$ = -28.5

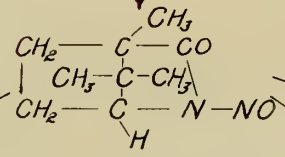


Amino Lauronic Anhydride
m.p. = 203°
$[\alpha]_D$ = -58



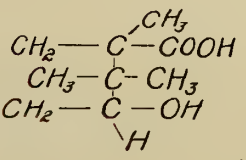
Hydrochloride
m.p. = 303°
$[\alpha]_D$ = +23°

↓



Nitroso Derivative.
m.p. = 138°-139°

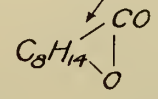
$C_8H_{13}COOH$
m.p. = 152°-154°



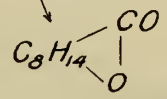
Hydroxy Lauronic

↓

Ethyl Ester
b.p. = 150° (30 mm.)
$[\alpha]_D^{33.5}$ = +6.73



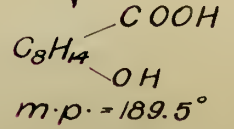
Iso Campholactone
m.p. = 32°
$[\alpha]_D^{28}$ = -63.1



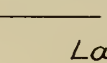
m.p. = 164°-165°
$[\alpha]_D^{22.4}$ = 13.87

Laurolene
b.p. = 120°-122°
$[\alpha]_D$ = -29.2; +22.9.

↓



m.p. = 189.5°



Lauronolic Acid
m.p. = 6.5°-8.°
$[\alpha]_D^{25}$ = 187.

↓

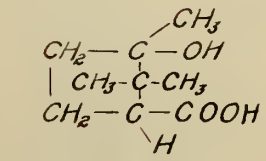
$C_8H_{15}COOH$
Dihydro Lauronolic.
b.p. = 215° (745 mm.)
$[\alpha]_D$ = 1.74

B. OR CAMPHOLYTIC SERIES.

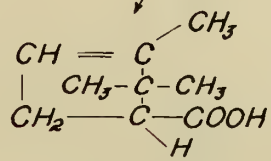
β. Camphoramidic Acid.

↓

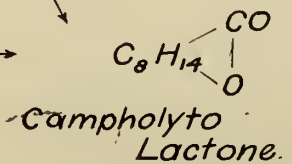
Amino-Dihydro-Campholytic Acid.



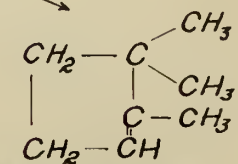
Dihydro Hydroxy Campholytic Acid
m.p. = 132°
$[\alpha]_D$ = 72.05



α. Campholytic Acid.
m.p. = liquid.
$[\alpha]_D$ = -61.5



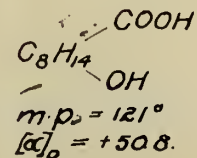
Campholyto Lactone.
m.p. = 115°-116°
$[\alpha]_D$ = +8.5



Iso Laurolene
b.p. = 108°-110°

Dihydro-Campholytic Acid
$[\alpha]_D^{28}$ = +44.9

β. Campholytic Acid.



m.p. = 121°
$[\alpha]_D$ = +50.8.

UNSATURATED ACIDS.

Thirteen unsaturated acids of the formula $C_8H_{13}COOH$, belonging to these two series, have been isolated and their properties studied. Eight of these, viz.,

l α -campholytic

d α -campholytic

r α -campholytic

i α -campholytic

campholytic

β -campholytic

Infra campholenic

camphoceenic

belong to the β or campholytic series. Five of them, viz.,

d lauronolic

r lauronolic

γ lauronolic

dehydro lauronic

and an unnamed, unsaturated acid obtained by Noyes and Taveau, belong to the α or lauronic series

- - - - -

l α -CAMPHOLYTIC ACID.

This acid was first obtained by Walker,[8] by the electrolysis of the sodium salt of the ortho (α) ethyl ester of camphoric acid. Noyes[9] obtained the same acid by treating dihydro-amino-campholytic acid with nitrous acid.

- -

8. J. Chem. Soc., 63, 495.
9. Am. Chem. J., 16, 505.

The density of the acid D = 1.0107

The specific rotation $(a)_D^{28} = -61.5$

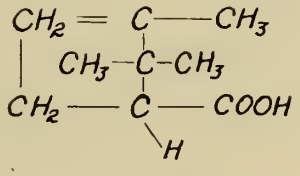
Dissociation constant K at 25° = 1.0×10^{-5}

Walker prepared the dibromide m. p. 110, and Noyes has prepared a semi-crystalline zinc salt, insoluble in water but easily so in ether.

On reduction, a dihydro campholytic acid is formed (page , this paper) which gives a rotation

$$(a)_D^{28} = +44.9$$

The synthesis of the acid by Perkin, Jun. and Thorpe[10] has definitely established its structure as



d - α CAMPHOLYTIC[11]

Noyes and Knight obtained this acid from isocamphoric acid, but in too small quantaties to make a satisfactory study of it.

$(a)_D = +46$

r CAMPHOLYTIC

This acid was prepared by the decomposition of the hydrobromide of campholytic with sodium hydroxide[12] m. p. 31° V. P. at 14 mm. = 127-128°

i - α CAMPHOLYTIC[13]

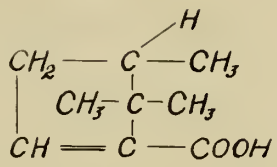
This acid was prepared from artificial camphor in exactly the same way as the active isomer described above. The amid melts at 99°. Dilute sulphuric acid converts it into the β campholytic.

- -

10. J. Chem. Soc., 85, 128
11. J. Am. Chem. Soc., 32, 1669
12. J. Chem. Soc., 77, 378; Am. Chem. J., 26, 285
13. Am. Chem. J., 27, 432

Δ^5 CAMPHOLYTIC[14]

By the reduction of the hydriodide of r α -campholytic acid a new dihydro campholytic acid was obtained. The action of an alcoholic solution of potassium hydroxide on the α Brom derivative of the dihydro acid gave a new campholytic acid, which differs from both α campholytic and infra campholenic in that it is not converted into β campholytic with dilute sulphuric acid. It is an inactive crystalline acid, m. p. 90-91, having the structural formula



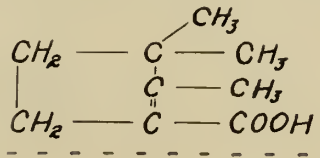
β CAMPHOLYTIC

By heating sulfocamphylic acid at 210-220° Koenig and Hoerlin[15] obtained a crystalline acid which melted at 135°. Since the analysis showed its formula to be the same as lauronolic acid, they called it isolauronolic acid.

Walker obtained a small amount of the same compound in the preparation of α campholytic, as described above, and called it camphothetic acid.

Noyes[16] obtained the acid from α campholytic by allowing it to stand for some time with hydrobromic or sulphuric acid or by boiling with dilute sulphuric. The identity of the acids of Noyes and Walker was established by Noyes from their conduct towards potassium permanganate, their melting point and crystalline structure. That of Noyes, and Koenigs and Hoerlin, from the melting point, and the fact that both give the same phenyl hydroxide, m. p. 199°.

The synthesis of this acid by Blanc has established the structure as



14. Am. Chem. J., 26, 289
15. Ber. 1893, 813
16. Am. Chem. J., 17, 428

The close relationship between α and β campholytic acids has been further demonstrated by Walker[17] and Noyes[18] since they have passed from the campholytic, through the hydrobromide to the α campholytic.

INFRA CAMPHOLENIC[19]

This acid is a viscous oil, V. P. at 145° = 24 mm., at 239° = 758 mm.; it is optically inactive and transformed by mineral acids into β campholytic. It differs from α campholytic in that it forms no hydrobromide, and its dibromide melts at 125°, while the dibromide of α campholytic melts at 110°.

CAMPHOCEENIC[20]

This is a crystalline acid obtained by Jagelki by the saponification with alcoholic potassium hydroxide, of the nitrile formed from camphenilonoxime, by the splitting off H_2O, m. p. 54°. Its relation to the active unsaturated acids has not been determined. Jagelki has given to it the formula given above for α campholytic, but this cannot be, since on treatment with dilute mineral acids it does not rearrange into β campholytic.

LAURONOLIC ACID[22]

This acid was first studied by Fittig and Woringer[21]. It is prepared by the decomposition of brom-camphoric acid anhydride with sodium carbonate.

$(a)_D^{25}$ = + 187.7; m. p. +6.5 -+8°; v. p. at 184° C = 100 mm.

r LAURONOLIC ACID[23]

r Lauronolic acid was prepared from artificial camphor by the same method

---

17. J. Chem. Soc., 77, 378
18. Am. Chem. J., 26, 282
19. J. Chem. Soc., 79, 108
20. Ber. 32, 1506.
21. Ann. 227, 6.
22. Page 24, this paper.
23. Page 32, this paper.

as the active isomer.

m. p. 5-8; v. p. at 192° = 100 - 102 mm.

γ LAURONOLIC

Walker[24] first prepared this acid by the electrolysis of the sodium salt of the allo (β) ethyl ester of camphoric acid, and gave to it the name allo-campholytic. Noyes[25] obtained the same acid by the decomposition of the chloride of amino-lauronic acid with sodium nitrite. The identity of the acids prepared by the two methods above mentioned has been definitely established by Noyes, since each forms

1. A calcium salt which crystallizes with two molecules of water.

2. A zinc salt, soluble in ether.

3. On treatment with dilute mineral acids, a lactone, m. p. 49-50°.

4. A liquid amid.

At 128-130° C. the acid has a vapor pressure of 10 mm.

$(a)_D^{20} = +118 - 146$

Since γ lauronolic gives a liquid amid where as the lauronolic of Fittig and Woringer gives a crystalline amid m. p. 72, it has been assumed that the two are not identical; by far the greater part of the evidence, however, seems to indicate that γ lauronolic is a mixture of the optically active isomers of lauronolic, identical with the acid obtained by the dry distillation of camphanic acid[26].

1. Each gives a positive rotation, which varies however within wide limits depending upon the conditions of preparation.

2. Each gives a calcium salt with approximately two molecules of water of crystallization.

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24. J. Chem. Soc., 67, 337
25. Am. Chem. J., 16, 508; 17, 433
26. Page 25, this paper.

3. Both exert the same vapor pressure at a definite temperature.

For γ lauronolic at 128-130° v. p. = 10 mm.

For lauronolic at 130-132° v. p. = 12 mm.

4. On warming with dilute mineral acids each gives the same lactone, m. p. 49-50°.

5. On treatment with bromine lauronolic acid gives a crystalline brom-lactone, m. p. 187°. From γ lauronolic acid Walker obtained a mixture of crystals and oil, the crystals melting at 184°. Tiemann obtained the same crystals, melting at 187°.

An impure amid obtained from lauronolic acid crystallizes only after standing for some time. The fact that a liquid amid was obtained from lauronolic acid is probably due to impurities present.

Bredt[27] states that the two acids are not identical since on oxidation of γ lauronolic he obtained camphoronic acid, whereas the oxidation of the lauronalic of Fittig and Woringer gave no trace of camphoronic; there is much reason to believe, however, that Bredt did not have a pure acid. He makes no mention of any products having been obtained other than camphoronic; but as may be seen above the decomposition of amino-lauronic acid is very complex and several products are obtained which have not been closely studied; some of these may on oxidation give camphoronic. On oxidation of γ lauronolic acid, Noyes obtained no trace of camphoronic.

DEHYDRO-LAURONIC

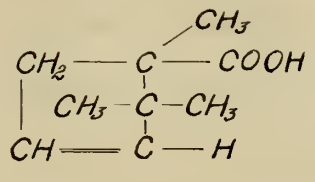
Bredt's lauronolic.

Bredt[28] prepared this acid from the diphenyl ester of α chlor-camphoric acid. This was first converted into the diphenyl ester of dehydro-camphoric acid by treatment with chinolin; by the dry distillation of this compound car-

27. Ber. 35, 1288
28. Ibid., 35, 1286

bon dioxide is evolved and the phenyl ester of the unsaturated mono basic acid obtained.

Since on oxidation it gives camphoronic acid its structure must be



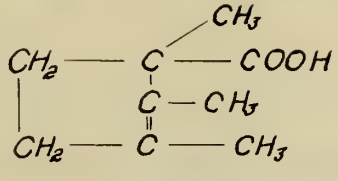
As this acid is an unsaturated derivative of lauronic acid, the only logical name for it seems to be dehydro-lauronic acid, which name is hereby suggested.

THE ACID OF NOYES AND TAVEAU

This acid was formed as one of the products of the decomposition of the nitroso derivative of the anhydride of amino-lauronic acid. It was purified by recrystallization of the calcium salt, m. p. 152-154°.

LAURONOLIC ACID

Lauronolic acid for which the structure



has been recently suggested by Eijkman, and which structure is substantiated by the work described in this paper, was first studied in 1885 by Fittig and Woringer. Some years previously Wreden[29] had obtained the acid but had made no detailed study of it. The compound was prepared in two ways; by the decomposition of brom-camphoric acid anhydride by boiling with water or dilute alkali and by the dry distillation of camphanic acid. The acids prepared in these two ways, Fittig and Woringer assumed to be identical since on standing

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29. Ann., 163, 330

with dilute mineral acid each rearranged giving the same lactone, m. p. 40-50°. From the acid they prepared the hydrobromide, an unstable crystalline product which decomposes, giving lauronolic acid and lactone, and a calcium salt which crystallizes with three molecules of water.

In 1894 Aschan[30] undertook the study of the acid in order if possible to throw light on the constitution of camphor; he prepared it in the two ways above mentioned, and like Fittig and Woringer, concluded that the two acids thus prepared were identical since each gave the same amid, m. p. 72°; and on treatment with the calculated amount of bromine in chloroform solution the same brom lactone.

Tiemann[31] first studied the optical properties of the acids prepared by the two methods above mentioned, and found that they differed widely in the rotation of the plane of polarized light. The acid obtained by the decomposition of the anhydride gave

$$(a)_D^{19} = +199$$

that from the distillation of the camphanic gave

$$(a)_D = +110 - - - +188.$$

Tiemann therefore proposed that the latter was probably a mixture of optical isomers. This fact we have conclusively proven by a comparison of the properties of three acids obtained by the following methods.

a. By the decomposition of active brom-camphoric acid anhydride with sodium carbonate.

b. By the dry distillation of camphanic acid.

c. An acid prepared from inactive (artificial camphor) in the same way as a above. For these acids the following properties have been observed.

- - - -

ROTATION

(a) From active anhydride	(b) From camphanic	(c) From inactive camphor
$(a)_D^{25} = +187.7$	$(a)_D = +63\text{-}180$	$(a)_D = 0$

DENSITY

(a)	(b) $(a)_D = +145.9$	(c)
$D_4^{25} = 1.0133$	$D_4^{25} = 1.0227$	$D_4^{25} = 1.0318$

VAPOR PRESSURE

(a)		(b) $(a)_D = +63$		(c)	
temp.	v. p.	temp.	v. p.	temp.	v. p.
184	100 mm.	188	100 mm.	192	100 mm.

INDEX OF REFRACTION. TEMP. 20 ± .2

	(a)	(b) $(a)_D = +63.9$	(c)
D	1.47586	1.47645	1.47655
C	1.47269	1.47349	1.47350
F	1.48323	1.48372	1.48372
G	1.48904	Invisible	1.50861

DISPERSION

	(a)	(b)	(c)
D-C	.00317	.00296	.00305
C-F	.01054	.01023	.01022

WATER OF CRYSTALLIZATION OF CALCIUM SALT

(a)	(b) $(a)_D = +63$	(c)
3 mols.	1.3 mols.	1 mol.

MELTING POINT

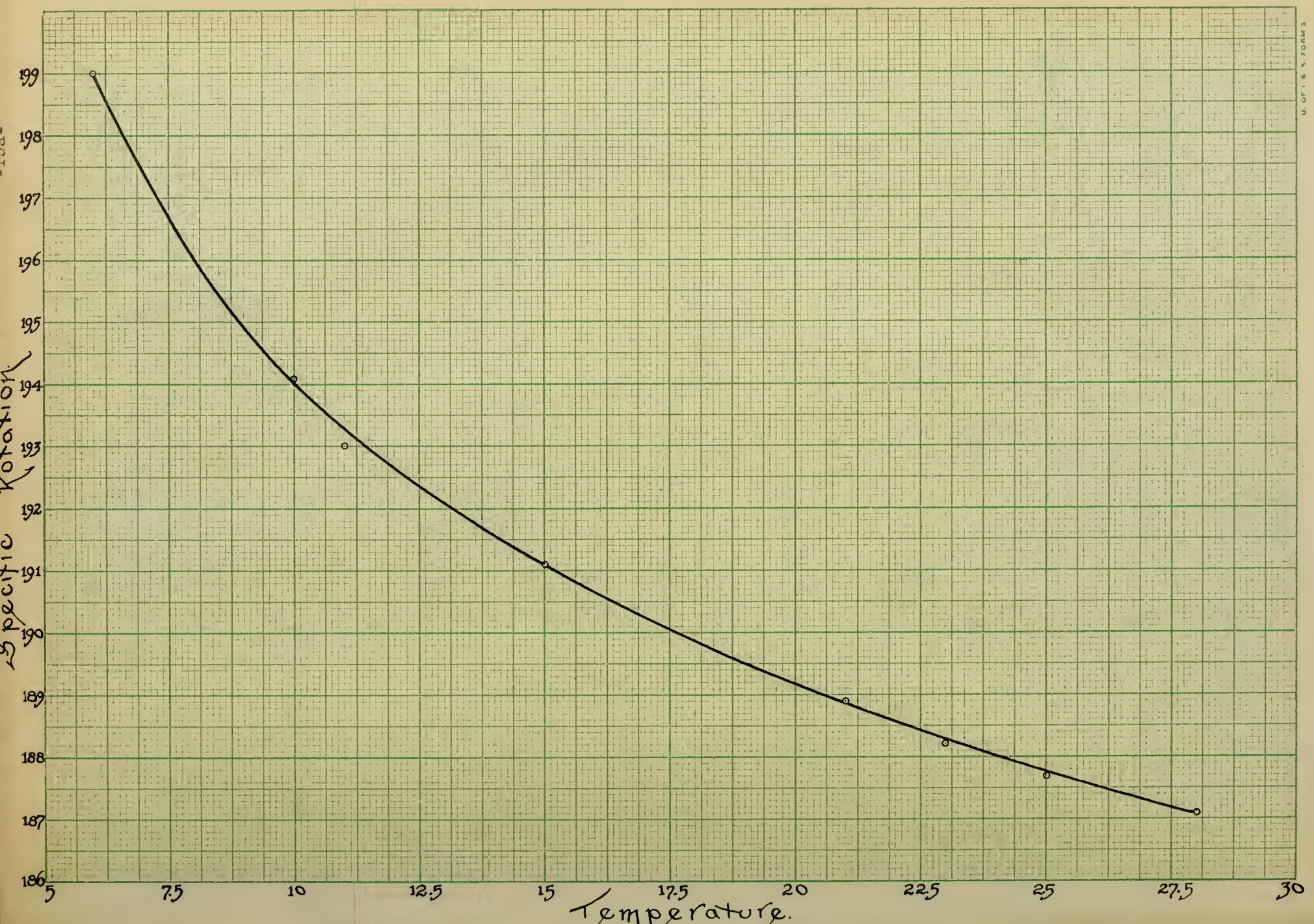
(a)	(c)
6.5 - 8	5 - 8

The dissociation constant K of the pure acid obtained from the decomposition of the anhydride = 1.36×10^{-5}

The influence of the temperature upon the rotation of the plane of polarized light by pure lauronolic acid is unusually great. The following specific rotations have been observed with the same sample of a pure acid in a 10 cm. tube.

temp.	$(a)_D$
28	187.1
25	187.7
23	188.2
21	188.9
15	191.1
11	193.0
10	194.1
6	199

This may be graphically represented by the following diagram.


199
198
197
196
195
194
193
192
191
190
189
188
187
186
Specific Rotation
5
7.5
10
12.5
15
17.5
20
22.5
25
27.5
30
Temperature.

When a mixture of the calcium salt of lauronolic acid and soda lime is distilled the hydrocarbon laurolene C_8H_{14}, b. p., 120-122° is obtained.

On treatment with phosphorus pentachloride and ammonia[32] the amid $C_8H_{13}CONH_2$ is obtained, m. p. 72°. A solution (10 per cent.) of the amid in ligroin gives a specific rotation varying from (a) = + 89.30 to + 94.61. The variation is probably due to the acid becoming more or less racemic during the process of preparation. An attempt to recover the acid from the amid by treatment with sodium hydroxide was unsuccessful.

The dihydro derivative[33] is formed by treating the acid with hydriodic a acid and subsequent reduction with zinc and absolute alcohol.

Rotation, $(a)_D^{25.5} = + 1.74$

Density, $D_4^{23.5} = 0.9008$

Index of Refraction

D = 1.45786

C = 1.45459

F = 1.46588

G = 1.47451

Dispersion

D-C = 0.00327

C-G = 0.01992

Vapor Pressure

At 215° C = 745 mm.

At 178° C = 100 mm.

The amid of dihydro-lauronolic acid has been obtained but not in sufficient quantity for careful purification. The crude amid melts at 50-51°.

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32. Page 29, this paper
33. Page 30, this paper

HYDROCARBONS

Two hydrocarbons of the formula C_8H_{14} are known; laurolene, a derivative of the lauronic series and isolaurolene, a derivative of the campholytic series. Both have been carefully studied and their structures definitely established by synthesis.

LAUROLENE

Laurolene has been obtained by the following methods.

1. By the slow distillation of camphanic acid either alone or in a current of carbon dioxide.[34] The amount of hydrocarbon obtained varies very considerable with the rate of distillation[35].

2. By the distillation of the unsaturated acid obtained by the electrolysis of the sodium salt of the allo (β) ethyl ester of camphoric acid[36] Walker found that a part of the product decomposed into laurolene and carbon dioxide, while the other part distilled constantly at 233-235° without decomposition. The undecomposed part was γ lauronolic; the part which decomposed was probably another acid of the same empirical formula. Pure lauronolic acid distills at atmospheric pressure without the formation of any hydrocarbon[37].

3. By the decomposition of amino-lauronic acid with nitrous acid[38].

4. By the decomposition of the nitroso derivative of the anhydride of amino-lauronic acid with sodium hydroxide[39].

5. By the distillation of calcium camphanate[40].

6. By the distillation of the calcium salt of lauronolic acid[41].

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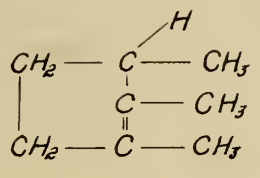
34. Wreden, Ann., 163, 330; Aschan, Ann., 290, 185; Zelinsky, Ann., 319, 311; Crossley and Renouf, J. Chem. Soc., 89, 27.
35. Page 34 , this paper.
36. J. Chem. Soc., 69, 749.
37. Page 28 , this paper.
38. Noyes, Am. Chem. J., 17, 432; Tiemann, Ber., 33, 2949.
39. Noyes and Taveau, Am. Chem. J., 32, 288; 35, 379.
40. Rupe and Maull, Ber., 26, 1202.
41. Page 29, this paper.

By four of the above mentioned methods, viz., 1, 2, 4, and 5 the hydrocarbon is formed in conjunction with lauronolic acid.

The rotation varies with the method of preparation from $+22.9^{\circ}$ to -29.2°[42]. From the study of its refractometric constants Eijkmann proposed for laurolene the structure



Much evidence from the chemical side in favor of this structure has been advanced by Noyes and Derick[43], and the synthesis of the compound by Noyes and Kyriakides[44] has definitely established it.

ISOLAUROLENE

The hydrocarbon isolaurolene has been prepared by distilling copper camphorate[45] by distilling the ammonium salt of sulphocamphylic acid[46] by heating β campholytic acid in a sealed tube at 340°[47], by heating β campholytic acid with anthracene[48], and by the action of alkali on the hydrobromide of campholytic acid[49]. Noyes has also obtained the hydrocarbon in very small quantaties from the decomposition of amino-dihydro-campholytic acid,

b. p. = $108\text{-}110^{\circ}$, $D^{15} = 0.7946$

Blanc[50] has synthesized the compound and thus definitely established its

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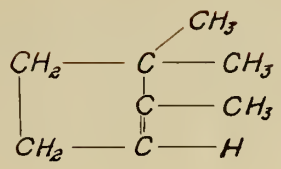
42. Crossley and Renouf, J. Chem. Soc., 89, 38; Noyes and Derick, J. Am. Chem. Soc., 31, 670.
43. J. Am. Chem. Soc., 31, 669; 32, 1061.
44. Ibid., 32, 1064
45. Moitessier, Jsb. Chem., 1866, 410.
46. Damsky, Ber., 20, 2959; Koenig and Meyer, Ber., 27, 3470.
47. Zelinsky, Ann. 319, 307; Blan, Bull, Chem. Soc., 19, 703
48. Crossley and Renouf, J. Chem. Soc., 89, 41
49. Walker and Cormack, J. Chem. Soc., 77, 379
50. Compt. rend., 142, 1084

structure as



LACTONES

Six lactones belonging to these two series have been isolated, but very little work has been done towards establishing their structures. Three of these, viz.,

ψ -campholactone

Inactive α campholactone

campholytolactone

belong to the campholytic series.

Three viz.,

campholactone

Iso-campholactone

an unnamed lactone

belong to the lauronic series.

ψ CAMPHOLACTONE

This was obtained, together with β campholytic acid by Lees and Perkin[51] by the action of aluminium chloride on camphoric anhydride. It was an oil which distilled constantly at 258° under ordinary conditions.

By treating with barium hydroxide two hydroxy acids were obtained, one melting at 113°, the other at 160°. This seemed to indicate that the original lactone was a mixture.

INACTIVE α -CAMPHOLACTONE

Perkin and Thorpe[52] obtained this lactone together with a number of other products by the action of magnesium methyl iodide on ethyl ketodimethylpentamethylenecarboxylate. It is an oil which distills at 155-157° under 50 mm. pressure.

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51. J. Chem. Soc., 79, 332.
52. Ibid., 85, 132

The corresponding hydroxy acid has the same structural formula as inactive α campholytic, since on treatment with dilute mineral acids it gives β campholytic acid.

CAMPHOLYTOLACTONE

Tiemann[53] obtained this lactone in small quantaties by the decomposition of dihydro-amino-campholytic acid with nitrous acid. Blanc[54] obtained the same compound with a much better yield by the distillation of α campholytic acid at ordinary temperatures.

m. p. 115-116°; v. p. at 105-108° = 8 mm. $(a)_D = + 8.5$

By boiling with alkali the corresponding hydroxy acid was obtained,

m. p. 121°; $(a)_D = + 50.8$

CAMPHOLACTONE

Campholactone is closely associated with lauronolic acid which on distilling under atmospheric pressure or on standing with mineral acids at ordinary temperature rearranges into the lactone form. It has also been obtained[55] by the dry distillation of camphanic acid, by warming at 100° lauronolic acid with dilute sulphuric[56], and in small quantities, in the preparation of dihydro-lauronolic acid[57].

Noyes[58] purified the lactone by converting into the barium salt of the corresponding hydroxy acid; it may also be very readily purified by recrystallization from ligroin[58],

m. p. 49-50°; $(a)_D = - 21.6$

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53. Ber., 33, 2938
54. Bull. soc. chim., 25, 81
55. Fittig and Woringer; Ann., 227, 10: Tiemann; Ber., 28, 2165: Aschan; Ber., 27, 2114
56. Noyes; J. Chem. Soc., 17, 434 ?
57. Page , this paper.
58. Page , this paper.

On warming with barium hydroxide and precipitating in the cold with hydrochloric acid, the corresponding hydroxy acid is obtained[59]. The hydroxy acid may be recrystallized from water.

m. p. 144-145°; $(a)_D = +16.0$

It is very unstable and easily decomposed, especially if warmed with dilute mineral acids, into lactone and lauronolic acid.

ISOCAMPHOLACTONE[60]

The decomposition of amino-lauronic acid with nitrous acid[61] or of the nitroso derivative of the anhydride of amino-lauronic acid with sodium hydroxide[62] gives isocampholactone together with a number of other decomposition products, m. p. 32°. The rotation in alcoholic solution (8.8 per cent), $(a)_D^{28} = -63.1$

THE UNNAMED LACTONE[63]

When the nitroso derivative of the anhydride of amino-lauronic acid is boiled with an aqueous solution of sodium hydroxide, there is formed besides a number of other products a lactone - melting point 164-165°, $(a)_D^{22} = +13.87$.

The corresponding hydroxy acid obtained by acidifying the barium salt melts at 189.5°.

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59. Ann., 227, 11; Ber., 33, 2946; Page , this paper.
60. J. Am. Chem. Soc., 31, 278; 32, 1665
61. Am. Chem. J., 17, 432
62. Ibid., 32, 285; 35, 379
63. Ibid., 35, 379

THE EFFECT OF RING FORMATION UPON THE ROTATION IN THE CAMPHOR SERIES.

It has long been known that ring formation, and the presence of an unsaturated union, has a very marked effect upon the rotation of the compound; as a general rule, either makes the rotation more positive[64]. Aschan[65] mentions the fact that camphoric anhydride forms an exception to this rule since it has a more negative rotation than camphoric acid.

By a comparison of the rotations of those compounds of this series, which may form ring structures, with the rotation of the ring compound, it may be seen that the majority of such compounds are exceptions to this rule; in only two cases does the formation of a ring make the rotation more positive. Thus it would seem that the formation of a ring has the general effect of making the rotation more negative.

camphoric acid

$(a)_D = + 49.7$

camphoric anhydride

$(a)_D = - 3.68$

inner anhydride

$(a)_D = -28.5$

amino-lauronic acid

$(a)_D = + 28.3$

amino-lauronic anhydride

$(a)_D = - 5.8$

hydroxy acid of campholyto-lactone

$(a)_D = + 50.8$

campholyto-lactone

$(a)_D = + 8.5$

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64. Haller and Desfontaines; Compt. rend., 136, 1613; 140, 1205; Walden; Z. physik. Chem., 20, 569.
65. Ber., 27, 2011

hydroxy acid of campholactone

$(a)_D = + 16.0$

campholactone

$(a)_D = - 21.6$

camphoamidic acid

α $(a)_D = + 45$

β $(a)_D = + 60$

camphoric imid

$(a)_D = - 10.6$

hydroxy α camphoramidic acid

$(a)_D = - 63.0$

camphanamid

$(a)_D = - 34.83$

amino-dihydro-campholytic acid

$(a)_D = + 57.3$

anhydride

$(a)_D = + 61.0$

Experimental Part

BROM CAMPHORIC ACID ANHYDRIDE

With some slight variations the method of Aschan[66] was followed. To 95 grams of pure, carefully dried camphoric acid in a 750 cc. flask, 200 grams of phosphorus pentachloride was carefully added, and the flask vigorously shaken, either in a good hood or better out of doors; after the first reaction which is somewhat violent, and the content of the flask is largely in the liquid condition, it was attached, by means of a paraffined, rubber stopper, to an upright condenser, and heated on a water bath for from 1-1/2 to 2 hours, or until all of the phosphorus pentachloride had passed into solution. After cooling, 29 cc. (slightly over one mol.) of dry bromine was slowly added, and again heated over a gently boiling water bath from 3 to 4 hours, or until the upper part of the flask had cleared, and there was no longer any evolution of hydrobromic acid.

The content of the flask was then divided into six or eight portions, each portion added to about six times its volume of ice water, and shaken vigorously until decomposition took place. We have found that by dividing the product in this way into several small portions, the decomposition not only takes less time, but the formation of a charry, resinous mass which so frequently forms when the whole product is decomposed in one flask, is avoided. The product was filtered, washed free from bromine and hydrobromic acid, and then digested for half an hour with 160 cc. glacial acetic acid and 40 cc. water; 300 - 400 cc. of water was then gradually added, and the heating continued for another half hour, being careful not to allow the temperature to

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66. Ber., 27, 3504.

rise over 70° C. The product was then filtered, washed free from acetic acid, mixed with alcohol, again sucked dry and quickly dried. This gave 92-93 grams of a very pure white anhydride, m. p. 215-216°. Any impure product was recrystallized from glacial acetic acid.

LAURONOLIC ACID AND CAMPHANIC ACID

To 100 grams of pure anhydride in a 750 cc. flask fitted with a Hopkin's condenser was added 300 grams of a 15 per cent. solution of sodium carbonate (45 grams Na_2CO_3) and boiled until the whole had passed into solution. When all was in solution, which required about 1-1/2 hours boiling, the content of the flask was filtered, 12-15 cc. dilute (1.1) sulphuric acid (enough to free the lauronolic but not the camphanic) added, and the lauronolic acid separated by steam distillation.

The distillate was saturated with sodium chloride, and the lauronolic acid extracted with ethyl ether. After drying the ethereal solution over sodium sulphate, the ether was distilled off and the product dried by passing a current of hydrogen for from thirty to forty minutes, keeping the acid at a temperature of from 60-65° and under as low a pressure as could be obtained with a water pump; usually 25-35 mm.

If dried in a current of air, or of carbon dioxide, decomposition soon begins and the product becomes black and tarry. With the current of hydrogen, however, we have found that the drying process may be continued indefinitely without any perceptible decomposition taking place. One hundred grams of the anhydride yields 9-10 grams of a yellowish colored acid. The crude acid gave a rotation

$$(a)_D^{28} = +180 - +183$$

Sufficient water was added to the residue from the steam distillation to make the volume up to about one liter, then 30 cc. dilute (1.1) sulphuric acid.

On cooling the camphanic acid crystallized out. About 55-60 grams of a fairly pure acid were obtained from 100 grams of anhydride. One crystallization from water gave a very pure acid, m. p. 200-201°.

LAURONOLIC ACID FROM CAMPHANIC ACID

By the distillation of camphanic acid in a slow current of carbon dioxide, a mixture of lauronolic acid, laurolene, campholactone and unchanged camphanic acid was obtained. The first three were separated from the camphanic by distillation with water vapor; as the hydrocarbon is extremely volatile it came over with the first few cubic centimeters of water and was thus easily separated. The rest of the distillate was made alkaline with sodium carbonate and the lactone extracted with ether. On acidifying the alkaline solution the lauronolic acid separated in oily drops and was extracted with ether and dried with a current of hydrogen in a manner similar to that of the lauronolic from brom camphoric acid anhydride.

PURIFICATION OF LAURONOLIC ACID

Much difficulty has been experienced in obtaining a pure lauronolic acid, owing first, to the ease with which the acid is decomposed; secondly, to the tendency on long standing at ordinary temperatures, or very wuickly at even moderately high temperatures, to rearrange into the racemic form.

The acid used in most of this work has been obtained from the purified calcium salt. This salt, which was obtained by neutralizing the acid with milk of lime is very difficultly soluble in water, and more soluble in cold than in hot, so that it could only be recrystallized by evaporating the solution. The solution was first purified by extracting with ether, then boiling for a short time with animal charcoal until it was perfectly colorless. On evaporation a

very pure salt separated on the surface of the solution in beautiful crystals. On analysis, they were found to contain three molecules of water, similar to the calcium salt of Fittig and Woringer.

The salt was decomposed with dilute hydrochloric acid and the pure lauronolic acid extracted with low boiling ligroin and dried under diminished pressure with a current of H, in the same manner as the crude acid,

$$(a)_D^{25} = + 187.7$$

An equally pure acid is obtained by distillation under diminished pressure with a Guericke pump if a sufficiently low pressure can be obtained. Under a pressure of 1/2 to 1 mm. it distills constantly at 104°. A thermometer in the Wood's metal bath registered 112-115°. It gave approximately the same rotation as that obtained from the calcium salt.

Under a pressure of 4-5 mm. it distills at 115-122° and gives a rotation

$$(a)_D^{25.5} = 187.3$$

The same acid was again distilled under pressure of 4-5 mm. and gave a rotation

$$(a)_D = 186.4$$

Thus showing a tendency to become racemic at this temperature.

CRYSTALLINE LAURONOLIC ACID

Fittig and Woringer[67] attempted to crystallize lauronolic acid, but state that while it became very viscous in a freezing mixture it would not crystallize. In a private communication Eijkman states that he has obtained it as a crystalline compound, but gives none of its properties.

The difficulty in getting the acid in crystalline form is evidently, not on account of the low melting point of the substance, but rather on account of

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67. Ann., 227, 8

the tendency to supercool. When left for some time in a freezing mixture of hydrochloric acid and finely ground ice, at a temperature of -23 to -20° it became very viscous but did not crystallize. With solid carbon dioxide and ether it forms a solid transparent mass, evidently simply the supercooled liquid, for on immersing in a freezing mixture at -20 it partly melts, then crystallizes into a solid, white mass.

By "seeding" the cooled acid the crystals were obtained in beautiful rosettes of long, concentric needles; the center of the rosette was slightly tinged with a green coloring matter, which seems to be characteristic of these compounds. The crystals melt at +6.5 to +8°.

PHYSICAL PROPERTIES

Under atmospheric pressure the acid distills at 230-235°, but the vapor pressure at this temperature cannot be accurately measured, owing to the formation of various oxidation and decomposition products. At lower temperatures the vapor pressure has been accurately measured by the method of Smith and Menzies[68], using a bath of pure paraffin.

At 184° v. p. = 99-100 mm.

The specific gravity has been determined by means of a small specific gravity bulb at various temperatures.

$$D_4^{28.5} = 1.0109$$

$$D_4^{25} = 1.0133$$

$$D_4^{10} = 1.0249$$

Tiemann[69] states that he has obtained a rotation of + 199 at 19° C. We have not been able to obtain as high a rotation at that temperature. In a 10 cm. tube, the acid recovered from the purified calcium salt gives a constant

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68. J. Am. Chem. Soc., 32, 897
69. Ber., 33,

specific rotation

$$(a)_D^{25} = 187.7$$

The index of refraction was determined for the sodium line D and the three hydrogen lines C, F, and G. The results for the three acids are given on page 12, this paper.

The electrical conductivity, determined with a saturated and a dilute solution, gave the dissociation constant $K = 1.36 \times 10^{-5}$.

DECOMPOSITION OF LAURONOLIC ACID INTO LAUROLENE AND CARBON DIOXIDE

Blanc[70] obtained isolaurolene from β campholytic acid by heating in a sealed tube at a temperature of 340°

$$C_8H_{13}COOH = C_8H_{14} + CO_2.$$

Since at such high temperatures molecular rearrangements readily occur, this method would have no value from the standpoint of structure. We have endeavored by keeping the acid at the boiling point to effect the same decomposition. After 1-1/2 hours the acid became very dark and somewhat viscous owing probably to the formation of oxidation products, but no hydrocarbon was formed. On distilling, all but a little resinous material came over at 200-230°. A considerable portion of the distilled product was insoluble in a solution of sodium carbonate. On extracting with ether and distilling off the ether this product was obtained in crystalline form, showing that a part of the acid had rearranged into the isomeric lactone.

To another portion of the pure acid a little zinc chloride was added before distilling. The larger part of the product distilled now at 120-125° and on redistilling came over constantly at 120-121°. This was evidently the

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70. Loc. cit.

hydrocarbon; it gave the following rotation

$$(a)_D^{30} = -5.36$$

The hydrocarbon was also obtained by mixing one gram of the calcium salt of lauronolic acid with soda lime and distilling. The distillate was again distilled with water vapor and the hydrocarbon separated from the first few cubic centimeters of aqueous distillate. Its boiling point at atmospheric pressure was 120-122°.

AMID OF LAURONOLIC ACID

To a small portion of the acid, cooled in ice water, one molecule of phosphorus pentachloride was gradually added. The reaction was immediate and somewhat vigorous. After completion the product was poured into ice water to decompose the oxychloride, and the chloride of the acid extracted with a little petroleum ether; concentrated NH_4OH was added to this ligroin solution and the product allowed to stand until it no longer smelled of ammonia. It was then extracted with ether, the ethereal solution dried over Na_2SO_4; and the ether distilled off; a dark oily mass remained which crystallized after standing for some time. On recrystallizing from water a very pure white crystalline product was obtained, which melted at 72°; 3.5 grams of acid yielded 1.1 grams amid. This was evidently identical with the amid of Aschan[71].

The amid gave the following rotation in a 10 per cent. ligroin solution.

$$(a)_D^{28} = 94.61$$

A nitrogen determination gave the following results

0.2342 grams amid gave 19.20 cc. nitrogen at 18°, 746 mm.

Calculated for $C_9H_{15}ON$	9.15 per cent. N
Found	8.96

71. Beilstein Handbuch der organischen Chemie (1) 708.

An attempt was made to saponify the amid; 0.5 grams was heated on a steam bath with 1.5 molecules (10 per cent. solution) sodium hydroxide for four hours. On acidifying and extracting with ether the unchanged amid was recovered.

The rotation would seem to indicate that the compound has become racemic. In the camphoric acids an amido group substituted for hydroxyl in the β carboxyl makes the rotation more positive, while if substituted in the α carboxyl it makes the rotation more negative. Similarly in camphanic acid an α substituted amido group makes the rotation more negative. Reasoning from analogy we would expect the rotation of lauronolamid to be more positive than that of the acid. Since, however, the rotation has dropped from + 187 to + 94.6 the compound has probably racemised. Another preparation of amid gave

$$(a)_D = 89.30$$

which also indicates racemisation. In the preparation of the amid some unchanged lauronolic acid was extracted with Na_2CO_3 and recovered. It gave a rotation

$$(a)_D = 167.9.$$

Thus showing that the product had racemised. Nothing further was done with the product.

DIHYDRO LAURONOLIC ACID

The hydrobromide of lauronolic acid has been prepared by Fittig and Woringer[72]. It is a very unstable product, which readily decomposes, giving the unsaturated acid and campholactone.

The crystalline hydriodide was prepared by passing hydriodic acid gas through a ligroin solution of lauronolic acid. Twelve grams of pure lauronolic acid in solution in low boiling ligroin was placed in a U tube, and a

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72. Ann., 227, 8

slow stream of hydriodic acid passed in as long as it continued to be absorbed. This required from 1 to 1-1/2 hours. The solution was then placed in a distilling bulb, and a current of air passed through at ordinary temperature until the ligroin was entirely evaporated. The iodide, which was thus obtained in the form of yellow plates was evidently very unstable, since on standing it continued to evolve fumes of hydriodic acid.

Various methods of reducing the iodide thus formed have been employed, with varying results. The zinc-copper couple, magnesium and alsohol, zinc dust and water, and zinc and hydriodic acid gave very poor results. The method which gave the best results and the one finally adopted was zinc and absolute alcohol. To the crystals of the iodide as obtained above some granulated zinc and absolute alcohol was added; although there was very little evolution of gas, the product immediately passed into solution; after standing for a short time a few cubic centimeters of a solution of hydriodic acid was added and more hydriodic acid gas passed through in order that any lauronolic acid which had been regenerated during the process might be reduced again. Finally some hydrochloric acid was added and a somewhat vigorous evolution of hydrogen maintained for some time. After diluting with water the dihydro acid was extracted with ligroin and the recovered acid treated with sodium carbonate to remove a small trace of lactone which formed. Any remaining unsaturated acid was oxidized in the alkaline solution with potassium permanganate and the dihydro acid separated from the oxidation products by steam distillation.

Twelve grams of lauronolic acid gave about three grams of the dihydro compound.

Analysis

0.1581 grams acid gave 0.4002 grams CO_2 and 0.1459 grams H_2O

Calculated for $C_8H_{15}COOH$	C	69.23	H	10.25
Found		69.03		10.24

Titration

The acid was titrated with N/0.0965 sodium hydroxide, using phenolphthalein as an indicator.

0.0588 grams acid required 3.85 cc. of NaOH for neutralization

Calculated 3.83

$D_4^{23.5} = 0.9008$

$(a)D^{25.5} = 1.74$

v. p. at $178^{o} = 100$ mm.

v. p. at $215^{o} = 749$ mm.

Index of refraction

D = 1.45786

C = 1.45459

F = 1.46588

G = 1.47451

Dispersion

D - C = .00327

C - G = .01992

The amid of dihydro lauronolic acid was prepared in the same way as the amid of lauronolic acid. It is exceedingly soluble in ether and has not been obtained in sufficient quantity to recrystallize. The crude product was washed with ether and dried on a porous porcelain plate, m. p. 50-51°.

INACTIVE LAURONOLIC ACID

The starting point of this preparation was artificial camphor obtained from the Ampère Electro-Chemical Company of New York. The camphoric acid and brom camphoric acid anhydride were prepared in the same way as the active compounds described above. The brom camphoric acid anhydride melted at 214°.

Mixed with the active anhydride it melted indefinitely, but about the same temperature.

On decomposing with sodium carbonate inactive lauronolic and inactive camphanic acids were obtained. The inactive camphanic melted at 199-200°. The lauronolic acid thus obtained like the active variety decomposed when distilled under ordinary conditions; it was purified by means of the Ca salt and also by distilling under diminished pressure.

0.1163 grams air dried salt lost 0.0060 grams H_2O at 100-110°

0.1355 grams salt lost 0.0067 grams H_2O at 100-110°

0.1848 grams salt lost 0.0103 grams H_2O at 100-110°

Calculated for 1 mol. of H_2O 4.95

Found (1) 5.1

(2) 4.95

(3) 5.05

0.1743 grams salt dried at 100° gave 0.0259 grams CaO

0.1200 grams salt dried at 100° gave 0.0138 grams CaO

Calculated for $(C_8H_{13}COO)_2Ca$ 11.56

Found (1) 10.62

(2) 11.54

On cooling the acid acts in the same way as the active variety. On standing in a freezing mixture at - 20° for some time the acid becomes very viscous but does not solidify. With solid CO_2 and ether it forms a transparent solid which in a mixture of ice and hydrochloric partly melts and then crystallizes. The crystals melt at 5-8°. The vapor pressure, specific gravity, rotation and index of refraction have also been determined in the same way as the active acid. (See page 12).

CAMPHANIC ACID

The method of preparing camphanic acid has already been described[73]. The pure acid melts at 200-201°.

$$(a)_D = -7.8$$

By distilling in a slow current of carbon dioxide, lauronolic acid, campholactone, laurolene and unchanged camphanic acid are obtained. The relative amount of each varies with the rate of distillation; by a rapid distillation we have obtained, from one hundred grams of camphanic acid, fifteen grams of laurolene; but by regulating the temperature so that the thermometer and the distilling bulb registered 130-140°, we have obtained as high as 28 grams of the hydrocarbon.

INACTIVE HYDROXY β CAMPHORAMIDIC ACID

To one gram of inactive camphoramidic acid, 5 cc. concentrated ammonium hydroxide was added and allowed to stand at room temperature for twelve hours. On acidifying with sulphuric acid a white crystalline precipitate was obtained which after recrystallization melted at 215°. A mixture of the compound with inactive camphanic acid melted at 155-160°.

Analysis

0.3044 grams of product gave 21.5 cc. nitrogen at 24°, 745 mm.

Calculated for $C_{10}H_{17}O_4N$ 6.51

Found 7.7

Various attempts to get the same product from active camphanic acid were unsuccessful.

BARIUM SALT OF HYDROXY CAMPHORIC ACID

This salt was very easily prepared by heating for 24 hours on the steam bath, camphanic acid, with an excess of barium hydroxide, and evaporated to

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73. Page , this paper.

dryness after precipitating the excess of barium. The yield is quantitative.

Analysis

0.2589 grams of salt gave 0.1596 grams $BaSO_4$

Calculated 36.25

Found 36.26

SILVER SALT OF HYDROXY CAMPHORIC ACID

By treating a solution of the barium salt with silver nitrate the corresponding silver salt is precipitated.

Analysis

0.2108 grams of salt gave 0.1070 grams of silver

Calculated 50.23

Found 50.75

ETHYL ESTER OF CAMPHANIC ACID

An attempt was made to get the diethyl ester of hydroxy camphoric acid by heating for one-half hour on the steam bath, the silver salt described above with two molecules of ethyl iodide. In every case, however, the ethyl ester of camphanic acid was obtained.

Analysis

0.2274 grams of ethyl ester gave 0.4785 grams CO_2 and 0.1661 grams H_2O

Calculated C 57.36 H 7.82

Found 57.34 8.09

Our product was evidently not quite pure since it melted at 53-55°. The pure ester melts at 58-63°.

$(a)_D$ = - 5.75 (20 per cent. etherial solution).

CAMPHANAMID

Camphanamid was prepared by the method of Auwers and Schnell[74] by allowing brom camphoric acid anhydride to stand for some hours with a concentrated solution of ammonium hydroxide. It was purified by recrystallizing from water.

m. p. 208° $(a)_D^{33} = -34.83$

HYDROXY α CAMPHORAMIDIC ACID

This was prepared[74] by boiling camphanamid for a short time with a solution of potassium hydroxide and acidifying, m. p. 155-156°.

The acid dried at room temperature gave a rotation

$(a)_D = -63.0$

On drying at 100° it lost one molecule of water of crystallization and gave a rotation

$(a)_D = -42.37$

ETHYL ESTER OF HYDROXY α CAMPHORAMIDIC ACID

The hydroxy α camphoramidic acid described above was distolved in a solution of sodium hydroxide, just neutralized with nitric acid, and the silver salt precipitated with silver nitrate.

The silver salt was heated for 4 hours on the steam bath with one molecule of ethyl iodide in alcoholic solution. After filtering and distilling off the alcohol, a resinous liquid and crystalline solid were obtained. The liquid was readily soluble in ether but the crystals rather difficultly so.

The solid product melted at 208-209° and gave the following analysis

0.2040 grams of product gave 13 cc. of nitrogen at 25°, 739 mm.

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74. Ber., 26, 1526

Calculated for $C_{12}H_{21}O_4N$ 5.76

Found 6.37

CAMPHOLACTONE

As stated above[75], lauronolic acid readily rearranges under certain conditions into the isomeric lactone. Much difficulty has been experienced, however, in getting the lactone in crystalline form, in sufficient quantities for study.

If lauronolic acid is heated with dilute mineral acid it chars and very little is obtained from the product. Fairly good yields have been obtained, however, by allowing the acid to stand for 12-24 hours with dilute hydrochloric acid, at a temperature of 40-50°. The unchanged acid and lactone was distilled with water vapor, the distillate made alkaline with sodium carbonate and the lactone extracted with ether. It is quite soluble in ligroin, but by cooling in a freezing mixture may be readily recrystallized from it.

m. p. 50° $(a)_D$ - 21.6 (10 per cent. alcoholic solution)

The lactone has been obtained in various ways from acids having widely differing rotations, but neither the method of preparation, nor the rotation of the acid from which it is prepared has any influence upon the rotation of the lactone.

HYDROXY ACID OF CAMPHOLACTONE

The lactone described above readily dissolves on warming with barium hydroxide, and the corresponding hydroxy acid is precipitated on acidifying. Fittig and Woringer obtained the acid as an oil which crystallized on standing; but by first cooling in ice water both the solution of the salt and the hydrochloric acid, we have obtained immediately on acidifying a beautiful crystalline precipitate of the hydroxy acid, m. p. 143. (Tiemann gives 144-

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75. Page 11 , this paper.

145 after recrystallizing from water).

$$(a)_D^{27} = + 16.0$$

DIHYDRO CAMPHOLYTIC ACID

This was prepared from α campholytic acid in the same manner as the dihydro lauronolic acid[76]

$$(a)_D^{28} = + 44.9$$

76, Page 30, this paper.

SYNTHESIS OF LAURONOLIC ACID

As a conclusion to the work described above an attempt has been made to synthesize lauronolic acid from laurolene through the following steps:-

$$C_8H_{14} + CH_3COCl + AlCl_3 = C_8H_{13}COCH_3 + HCl + AlCl_3$$

$$2C_8H_{13}COCH_3 + 6NaOCl = 2C_8H_{13}COCCl_3 + 6NaOH$$

$$2C_8H_{13}COCCl_3 + 2NaOH = 2C_8H_{13}COONa + 2CHCl_3$$

Although owing to lack of time this work has not been carried to a definite and satisfactory conclusion it seems advisable to give a statement of it here.

Thirty grams of aluminium chloride, 60-75 grams of dry low boiling ligroin[±], and 22 grams of laurolene were placed in a large flask, and 20 grams of acetyl chloride added, a few drops at a time and with continual shaking. The shaking was continued for some time after all the acetyl chloride had been added, until the evolution of gas had practically ceased.

The content of the flask was now in two layers, the upper of which after washing with water was found to consist of practically pure ligroin. The lower layer was decomposed by pouring into cold water, extracted with ligroin, and the ligroin extract fractionally distilled under diminished pressure. At 35 mm. pressure about 1 gram came over below 95°; 8 to 9 grams from 95-105°; and 6-8 grams at 185-200°. The middle portion was redistilled and about 7 grams obtained which distilled constantly at 98-103° (35 mmm. pressure).

By treating this fraction with phenyl hydrazine a dark oily mass was obtained, probably a hydrazone. With semi-carbazine a white crystalline product was obtained, which after several recrystallizations from dilute alcohol melted at 193°.

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± This reaction has also been carried through with carbon bisulfid, but we have obtained a much cleaner reaction and better yield with ligroin.

Analysis

0.1617 grams of compound gave .3734 grams CO_2 and .1419 grams H_2O

Calculated for $C_{11}H_{19}ON_3$ C 63.15 H 9.09

Found 62.95 9.70

By warming the semi-carbazone with dilute hydrochloric acid a quantitative yield of the ketone was recovered. Under 35 mm. pressure it distilled constantly at 98-100°, giving perfectly colorless oil.

Analysis

0.1760 grams of ketone gave 0.5056 grams CO_2 and 0.1706 grams H_2O

Calculated for $C_{10}H_{18}O$ C 78.95 H 10.52

Found 78.35 10.73

Rotation

(a) = + 1.87

Index of refraction at 20° ± .2

D = 1.46384

C = 1.46057

F = 1.46960

G = invisible

Dispersion

D-C = .00327

By treating the ketone with sodium hypochlorite two products have been obtained; a crystalline solid, m. p. 63, and a dark oily liquid. The liquid reacts acid towards litmus, readily reduces potassium permanganate and forms a slightly soluble calcium salt. The calcium salt has not been obtained in sufficient quantity for careful purification. The analysis of the crude salt gave

0.1318 grams salt lost .0066 grams H_2O at 100-110° and gave

0.0728 grams $CaSO_4$

Calculated for 1 mol. of water	4.95
Found	5.07
Calculated for $(C_8H_{13}COO)_2Ca$	11.56
Found	16.7

The crystalline product has not been studied.

Since the calcium salt of inactive lauronolic acid crystallizes with one molecule of water of crystallization, these results would indicate that lauronolic acid has been formed. This part of the work will be continued.

Structure of

LAURONOLIC ACID

Although both brom camphoric acid anhydride and camphanic acid retain the gem dimethyl group the following evidence points to the fact that in lauronolic acid one methyl group has wandered, thus forming a 1.2.3. trimethyl compound as suggested by Eijkman.

By distilling a mixture of the calcium salt of lauronolic acid and soda lime an almost quantitative yield of the hydrocarbon laurolene is obtained, and this has been proven by synthesis to contain a 1.2.3. trimethyl group.

If the double bond were in the Δ^3 position we would have an acid identical with dehydro lauronic, which on oxidation ought to give camphoronic acid. Oxidation of lauronolic acid, however, gives no trace of camphoronic acid[77].

A comparison of the dissociation constants of lauronolic acid and campholytic acid shows that, while the difference is not very great, the lauronolic gives a distinctly higher value for K. This is difficult to explain if the unsaturation in each is Δ^3. It has been shown, however[78], that in both open chain and ring unsaturated acids a Δ^2 unsaturation invariably gives a greater dissociation constant than Δ^1 or Δ^3. This would indicate that the double bond is Δ^2.

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77. Tiemann; Ber., 33, 2949; Bredt; Ber., 35, 1288
78. Derick; J. Am. Chem. Soc., 32, 1339.

At the present stage of our knowledge of the effect of structure upon the optical rotation it is difficult to explain the high, positive rotation of lauronolic acid, or to draw any positive conclusions as to its structure from its optical properties. It has been shown, however, by comparison of the rotations of a large number of compounds[79] that an unsaturated bond increases the rotatory power and that the effect is greater the nearer the unsaturated bond is to the asymmetric carbon atom. This again, however, would seem to indicate that in lauronolic acid the double bond is nearer the asymmetric carbon atom than in α campholytic.

We can get some idea of the effect of the double bond upon the rotation by comparing the rotations of the unsaturated and saturated acids in each series.

lauronolic acid	dihydro lauronolic acid
$(a)_D = + 187.7$	$(a)_D = + 1.74$

campholytic	dihydro α campholytic
- 61.5	+ 44.9

Thus in lauronolic acid the double union seemingly makes a difference of 185.96° while in α campholytic it makes a difference of only 106.4°. Although these rotations have been found fairly constant for several samples a part of the difference may be due to the saturated compound becoming more or less racemic in the process of preparation.

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79. Walden; Z. physik. Chem., 20, 569: Zelinsky; Ber., 35, 2494, 2682; Rupe; Ann., 327, 157: Haller and Desfontaines; Caompt. rend., 136, 1613; 140, 1205.

Biographical

The writer received his early education in the grade schools and Collegiate Institute of the city of Brantford, Canada, and his university training in McMaster University, Toronto. From the latter institution he received the degree of Bachelor of Arts in 1907, with majors in chemistry and biology.

During the academic years 1907-08 and 1908-09 he taught chemistry and physics in Woodstock College, an academic department of McMaster University, and at the same time pursued post-graduate work in organic chemistry under Professor J. Bishop Tingle with whom he published the following paper-

"Nitraniline Derivatives of Organic Acids". J. Am. Chem. Soc., 31, 1312

In 1909 he received the degree of Master of Arts from McMaster University, and the same year entered the University of Illinois on a fellowship, which he has held during the academic years 1909-10; and 1910-11.

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